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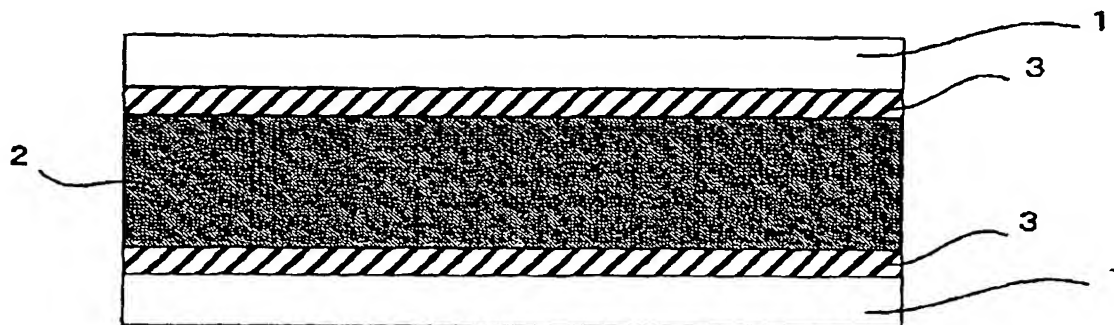
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(54) Title: METHOD OF PRODUCING LAMINATES, AND LAMINATES



(57) Abstract: In view of the above discussed state of the art, it is an object of the present invention to provide a method of producing a laminate excellent in insulation and adhesion strength between a functional material and conductive material sandwiching that, without needing any organic solvent in production thereof, and laminates produced thereby. A method of producing a laminate which comprises the step (1) of forming, on each of two conductive materials, an adhesive resin layer by an electrodeposition step with a cationic electrodepositable adhesive composition comprising a cationic resin composition and the step (2) of joining the adhesive resin layer on each conductive material as obtained in the step (1) to each side of a functional material.

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DESCRIPTION  
METHOD OF PRODUCING LAMINATES, AND LAMINATES

TECHNICAL FIELD

5           The present invention relates to a method of producing laminates, and to laminates.

BACKGROUND ART

10           In the field of electronic materials, a plurality of conductive materials are joined together via an insulating layer(s), or a conductive material is joined to a functional material via an insulating layer. The formation of such an insulating layer is required in such fields of application as printed circuit boards and capacitor films, for instance. Used  
15           as the insulating layer in such electronic materials field are layers of a polyimide resin, polyamide resin or polyamideimide resin having good heat resistance and insulating properties.

          Such a polyimide resin, polyamide resin or polyamideimide resin may also be used as an adhesion layer for the formation  
20           of a laminate in the field of electronic materials. As the method of adhesion using such resins, there is known such a technology which comprises, for example, dissolving these resins in an organic solvent, applying the resulting composition to an adhesion surface, and adhering the resulting  
25           adhesive layer to an adherend surface.

          The thus-formed adhesive layer simultaneously functions as a layer having an excellent insulating property and a heat resistance.

          However, polyimide resins, polyamide resins or  
30           polyamideimide resins are indeed excellent in insulating properties and heat resistance but, in adhesive layer formation, they require the use of an organic solvent such as N-methylpyrrolidone. The use of such an organic solvent is undesirable from the environmental viewpoint. Further, in  
35           certain cases, the organic solvent may remain in adhesive layer,

so that leading to the insulation deterioration and insufficient levels of adhesion strength in the case of adhesion of metal layers.

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#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic illustration of a laminate producible by the method of producing a laminate of the invention.

10 Fig. 2 is a chart showing the results of XPS measurements.

#### Explanation of Numerals

- 1. conductive material
- 2. functional material
- 15 3. adhesive resin layer

#### SUMMARY OF THE INVENTION

In view of the above discussed state of the art, it is an object of the present invention to provide a method of  
20 producing a laminate excellent in insulation and adhesion strength between a functional material and conductive material sandwiching that, without needing any organic solvent in production thereof, and laminates produced thereby.

The present invention provides a method of producing a  
25 laminate

which comprises the step (1) of forming, on each of two conductive materials, an adhesive resin layer by an electrodeposition step with a cationic electrodepositable adhesive composition comprising a cationic resin composition  
30 and the step (2) of joining the adhesive resin layer on each conductive material as obtained in the step (1) to each side of a functional material.

Preferably, the cationic electrodepositable adhesive composition is substantially incapable of generating any  
35 volatile component in the step of heating for curing.

The above-mentioned cationic resin composition is preferably an unsaturated bond-containing one.

The cationic resin composition is preferably one allowing the formation, in the adhesive resin layer, of such chemical species activated by the electrode reaction caused by voltage application in the electrodeposition step as can promote the progress of the curing reaction.

The cationic resin composition is preferably a sulfonium group- and propargyl group-containing one.

10 The cationic resin composition preferably has a sulfonium group content of 5 to 400 millimoles, a propargyl group content of 10 to 495 millimoles, and a total content of sulfonium and propargyl groups of not more than 500 millimoles, per 100 g of the solid matter in the cationic resin composition.

15 The cationic resin composition preferably has a sulfonium group content of 5 to 250 millimoles, a propargyl group content of 20 to 395 millimoles, and a total content of sulfonium and propargyl groups of not more than 400 millimoles, per 100 g of the solid matter in the cationic resin composition.

20 The cationic resin composition preferably has an epoxy resin as a skeleton.

The epoxy resin is preferably a novolak cresol epoxy resin or novolak phenol epoxy resin and has a number average molecular weight of 700 to 5,000.

25 The method of producing a laminate preferably comprises a step of drying between the step (1) and step (2).

The step (2) preferably comprises a step of adhesion with heating and a step of curing by heating.

30 The functional material is preferably made of an organic or inorganic material.

The present invention is also concerned with a laminate obtained by the above-mentioned method of producing a laminate.

#### DETAILED DESCRIPTION OF THE INVENTION

35 In the following, the present invention is described in

detail.

The laminate produced by the method of producing a laminate according to the invention has a structure shown in Fig. 1, for instance. The laminate shown in Fig. 1 comprises a functional material 2 having, on each side thereof, a conductive material 1 adhered thereto via an adhesive resin layer 3. Since the adhesive resin layer 3 can also serve as an insulating layer simultaneously, the method of producing a laminate according to the invention can be advantageously applied in those cases where it is required that conductive materials 1 and a functional material 2 be joined together in an electrically insulated state.

The first step in the method of producing a laminate according to the invention is the step in which an adhesive resin layer is formed on each conductive material by an electrodeposition step with a cationic electrodepositable adhesive composition comprising a cationic resin composition. Thus, the step (1) is a step of forming an adhesive resin layer on the surface of each conductive material by carrying out a cationic electrodeposition step using a cationic electrodepositable adhesive composition to obtain a conductive material having an adhesive resin layer on the surface thereof. According to the method of producing a laminate in accordance with the invention, adhesive resin layers are formed by an electrodeposition step and, therefore, it is unnecessary to use any organic solvent and the load on the environment can thus be reduced.

The cationic electrodepositable adhesive composition used in the above step (1) comprises a cationic resin composition. By carrying out the electrodeposition step [step (1)] using the cationic resin composition and further carrying out the adhesion step [step (2)], it is possible to cause manifestation of excellent adhesiveness.

Unlike the conventional nonaqueous adhesives, the cationic electrodepositable adhesive composition used in the

above step (1) is a water-based (water-thinned) adhesive and, therefore, the use of VOCs, environmental hormones and other environmental problem substances can be restrained. Further, in spite of its being a water-based adhesive, it can give  
5 adhesive layer at least comparable in insulating properties to the layer formed by the conventional adhesives.

Since the cationic electrodepositable adhesive composition used in the above step (1) is applied by an electrodeposition step, it is easy to form a closed system  
10 suppressing occurrence to the loss of the adhesive ; as a result, the emission of industrial waste can be reduced as well.

The above cationic electrodepositable adhesive composition can be applied by an electrodeposition step and, therefore, they can be uniformly applied onto substrates having  
15 conductivity and can uniformly form an adhesive resin layer comprising a cationic resin composition on each substrate.

Since it is a method involving application by an electrodeposition step, the above-mentioned method of producing a laminate is superior in productivity and economy  
20 and is a method relatively low in running cost.

The above-mentioned cationic resin composition is preferably one having functional groups capable of causing interaction with the metal atoms in the conductive material surface on the occasion of adhesion. Thus, the cationic resin  
25 composition is preferably one such that when the step (1) and step (2) are carried out, interaction takes place between the functional groups in the cationic resin composition and the metal atoms in the conductive material surface. Such a property enables firm adhering of the adhesion resin layer formed on each  
30 conductive material to the conductive material surface. Although the interaction between the functional groups in the cationic resin composition and the metal atoms in the conductive material surface in such a firmly adhered state is not clear, it is supposed, in view of the results of XPS (X-ray  
35 photoelectron spectroscopy) measurements, that there is a state

like a covalent bond formed between the functional group in the cationic resin composition and the metal atoms in the conductive material surface. The formation of such a state leads to an improvement in the adhesion strength between the adhesive layer and conductive material surface and, thus, the intended adhesion can be performed without subjecting the conductive material surface to any special surface treatment. While the particulars of this mechanism are not certain, it is presumable that chemical species are electrolytically formed in the adhesion resin layer and those chemical species form a covalent bond-like state with metal atoms in the conductive material surface or promote the formation of such a covalent bond-like state. As the functional groups, there may be mentioned, for example, a sulfonium group and so forth.

The occurrence of a covalent bond-like state formed between the above functional group and metal atoms in the conductive material surface can be confirmed, for example, based on the chemical shift of the 2p orbit sulfide sulfur atom as measured by XPS.

The cationic electrodepositable adhesive composition to be used in the above step (1) is preferably such one that will not allow the substantial emission of any volatile component in the step of heating for curing. When an adhesive resin layer is formed by an electrodeposition step using a cationic electrodepositable adhesive composition and the adhesive resin layer is further cured by heating, the vehicle component constituting the adhesive resin layer may partly evaporate in the step of curing in some instances. The emission of such volatile component may cause a decrease or unevenness in adhesion strength and/or in insulating property. The emission of a volatile component is unfavorable from the environmental viewpoint as well. Since there is no substantial volatile component emission from the above-mentioned cationic electrodepositable adhesive composition in the step of curing by heating, the above problems will not arise.

The phrase "there is no substantial volatile component emission" as used herein means that such a volatile component as naturally expected to be emitted in view of the curing reaction will not be emitted. In a curing system in which a blocked isocyanate is used as a curing agent, for instance, it is naturally anticipated, in view of the curing reaction, that the blocking agent will be emitted as the volatile component and, in a curing system in which curing is attained by a condensation reaction, it is anticipated that a volatile component resulting from the condensation reaction will be emitted. The cationic electrodepositable adhesive composition allowing no substantial volatile component emission therefrom comprises a cationic resin composition of which no such volatile component emission can be expected. The cationic electrodepositable adhesive composition can be rendered substantially incapable of emitting any volatile component by selecting an appropriate curing system. The volatile component emission-free curing system is not particularly restricted but includes, among others, the propargyl/allene curing system, the curing system involving the Michael addition of an active methylene group to an  $\alpha,\beta$ -unsaturated bond, and the oxidative polymerization curing system.

The cationic resin composition to be used in the above step (1) is preferably an unsaturated bond-containing one. Thus, the adhesion resin layer formation is realized by the curing reaction involving polymerization of the unsaturated bond. By this, the emission of volatile components in the step of curing can be reduced, and the adhesion strength and/or insulating properties can be prevented from being decreased or becoming uneven due to the occurrence of a volatile component(s). Such unsaturated bond is not particularly restricted but may be any of those capable of forming curing systems in which the reaction progresses as a result of polymerization of the unsaturated bond. It includes, among others, those



unsaturated bonds which form the propargyl/allene system, curing systems involving the Michael addition of an active methylene group to an  $\alpha,\beta$ -unsaturated bond, and oxidative polymerization curing systems.

5       The "unsaturated bond" so referred to herein means a carbon-carbon double bond or a carbon-carbon triple bond.

      The cationic electrodepositable adhesive composition to be used in the above step (1) is preferably one such that activated chemical species are formed in the adhesion resin  
10 layer by the electrode reaction induced by voltage application in the step of electrodeposition and the activated chemical species promote the progress of the curing reaction.

      Thus, for promoting the curing reaction in the adhesion resin layer, it is desirable that an electrochemical reaction  
15 is induced in advance in the electrodeposition step by voltage application; and, since the progress of the curing reaction is by nature very slow upon mere heating alone, the curing reaction will not proceed in the bath even upon exposure to the Joule heat generated by voltage application, and this is favorable  
20 from the bath stability viewpoint. The "progress of the curing reaction" means that a cured film is actually obtained by the curing reaction. Therefore, in cases where the curing reaction occurs as a chemical reaction but no cured film can be obtained, the curing reaction is regarded as making no progress.

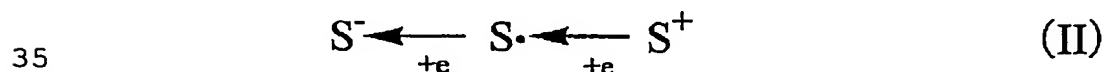
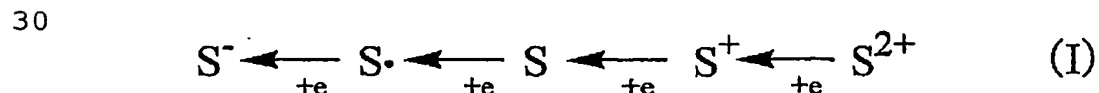
25       Such properties as mentioned above are owing to the generation of chemical species activated by an electrode reaction involving donation and acceptance of electrons on the occasion of adhesion resin layer formation following voltage application to the conductive material and to the involvement  
30 of those chemical species in the progress of the reaction for curing the adhesion resin layer.

      Such properties as mentioned above are illustrated more specifically. The above-mentioned activated chemical species are generated in the adhesion resin layer as radicals for  
35 causing the curing of the adhesion resin layer or as species

capable of readily causing the generation of such radicals, for instance, and promote the progress of the curing reaction and other reactions. In cases where the adhesion resin layer curing reaction is initiated in the step of heating for curing, that  
 5 activated state is maintained until the step of heating for curing.

When the cationic electrodepositable adhesive composition is used in the above step (1), both the electrodeposition step and heating step govern the curing of  
 10 the adhesion resin layer. Thus, in the electrodeposition step, the adhesion resin layer is formed and, simultaneously, one or more curing system-constituting essential components are formed to constitute a complete curing system, whereby the adhesion resin layer is prepared for the progress of the curing  
 15 reaction. In the subsequent heating step, the adhesion resin layer curing reaction proceeds with the help of the curing system completed in the electrodeposition step until completion of the curing. It is a matter of course that the curing reaction can be initiated not only in the heating step but also in the  
 20 electrodeposition step once the curing system-constituting essential components have been formed.

The mechanism of the electrode reaction in the cationic electrodepositable adhesive composition used in the above step (1) as induced by voltage application in the electrodeposition  
 25 step is represented by the formula (I) or (II) shown below. In the electrodeposition step, the electrode reaction occurs when electrons are donated to the functional groups which the substance (substrate; represented by "S" in the formula) deposited on the electrode has.



In the reactions represented by the above formulas (I) and (II), the activated chemical species mentioned above are anions and radicals formed in the above reactions. These can be independently involved in the progress of the curing reaction, and two or more species, too, can combinedly provide the same properties. Here, more specifically, the above anion is formed as an electrolytically generated base resulting from electrochemical changes, by the electrode reaction, of the corresponding component contained in the above cationic electrodepositable adhesive composition. On that occasion, strong interaction presumably takes place between the anion formed and the substrate, i.e. metal atoms in the conductive material surface, leading to the formation of a covalent bond-like state.

Since the reactions represented by the above formulas (I) and (II) can be controlled by means of the magnitude of the electrode potential in the above electrode reactions, it is possible to produce the above-mentioned activated chemical species in amounts as needed by controlling the electrode potential.

The above-mentioned electrolytically generated base and radical are not particularly restricted but includes, among others, those generated when a voltage is applied to an onium group, such as an ammonium, sulfonium or phosphonium group, as a supporting electrolyte. When the onium group holds a hydroxide ion formed upon voltage application, it becomes an electrolytically generated base. This electrolytically generated base occurs in the above-mentioned adhesive resin layer and is involved in the curing of the adhesive resin layer. The above onium group can form a radical in the vicinity of the electrode, and this radical, too, can be involved in the curing of the adhesive resin layer mentioned above.

When, for example, an onium group as a hydratable functional group is contained in the base resin, a pigment dispersing resin or some other resin component, or an onium

group-containing compound is added as a component other than resin components, the above cationic electrodepositable adhesive composition can provide the activated chemical species in the above electrode reactions.

5       The above cationic resin composition is preferably a sulfonium group- and propargyl group-containing one.

      The sulfonium group, which is an anionic group, in the above-mentioned sulfonium group- and propargyl group-containing cationic resin composition is activated by the electrode reaction induced by voltage application in the electrodeposition step and serves as an origin of radical or anion generation to thereby promote the progress of the curing reaction, and strong interaction takes place between the sulfur atom of the sulfonium group and metal atoms in the conductive material surface, leading to the formation of a covalent bond-like state. The propargyl group causes a curing reaction by polymerization of its unsaturated bond, hence the curing reaction does not generate any volatile component. Further, the reaction of the propargyl group is promoted by a radical or anion derived from the sulfonium group activated by the electrode reaction induced by voltage application in the electrodeposition step. In this way, these two functional groups can efficiently satisfy all the plurality of functions required of the cationic resin composition. Further, the covalent bond-like state resulting from the interaction between the sulfur atom of the sulfonium group and metal atoms in the conductive material surface is formed efficiently and the intensity of the interaction is high, so that the adhesion strength can be improved. Furthermore, the coating films formed from a cationic electrodepositable adhesive composition comprising the above-mentioned cationic resin composition have good insulating properties.

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      When the above-mentioned cationic electrodepositable adhesive composition to be used in the above step (1) comprises a sulfonium group- and propargyl group-containing one, the

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component resins of above cationic resin composition may have both a sulfonium group(s) and a propargyl group(s) in each molecule, but this is not absolutely necessary. Thus, for example, the component resins may have only a sulfonium group(s) or only a propargyl group(s) in each molecule. In the latter case, however, the whole resin composition should have both of these two kinds of curable functional groups. Thus, the resin composition may comprise any of sulfonium group- and propargyl group- containing resin, a mixture of a resin having only a sulfonium group(s) and a resin having only a propargyl group(s), and a mixture of all of said kinds of resins. It is herein defined in the above sense that the resin composition has both a sulfonium and a propargyl group(s).

The sulfonium group mentioned above is a hydratable functional group in the above resin composition. When an electric voltage or current exceeding a certain level is applied to the sulfonium group in the electrodeposition step, the group is electrically reduced on the electrode, whereby the ionic group disappears, resulting in irreversible passivation. This is presumably the reason why the above cationic electrodepositable adhesive composition can manifest a high level of throwing power.

It is considered that, in this electrodeposition step, the electrode reaction provoked generates the hydroxide ion, which is held by the sulfonium ion, with the result that an electrolytically generated base is formed in the adhesive resin layer. This electrolytically generated base can convert the propargyl group occurring in the adhesive resin layer and being low in reactivity upon heating to the allene bond high in reactivity upon heating.

The resin to serve as the skeleton of the above cationic resin composition is not particularly restricted but an epoxy resin is suitably used.

Suited for use as the epoxy resin are those having at least two epoxy group within each molecule, including, for example,

such epoxy resins as epi-bis-epoxy resins, modifications thereof resulting from chain extension with a diol, dicarboxylic acid or diamine, for instance; epoxidized polybutadiene; novolak phenol polyepoxy resins; novolak cresol polyepoxy resins; polyglycidyl acrylate; polyglycidyl ethers of aliphatic polyols or polyethers polyol; and polyglycidyl esters of polybasic carboxylic acids. Among them, novolak phenol polyepoxy resins, novolak cresol polyepoxy resins and polyglycidyl acrylate are preferred because of the ease of polyfunctionalization for increasing curability. The above epoxy resin may partly comprise a monoepoxy resin.

The above cationic resin composition preferably comprises any of the above-mentioned epoxy resin as a skeleton resins, with a number average molecular weight of 500 (lower limit) to 20,000 (upper limit). When the molecular weight is less than 500, the coating efficiency in the electrodeposition step will be poor and, when it exceeds 20,000, any good adhesive resin layer will be formed no longer on the conductive material surface. The number average molecular weight can be selected within a more preferred range according to the resin skeleton. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, the lower limit is preferably 700 and the upper limit is preferably 5,000.

The sulfonium group content in the above cationic resin composition should satisfy the condition concerning the total content of the sulfonium and propargyl groups, which is to be described later herein, and, in addition, the lower limit thereto is preferably set at 5 millimoles and the upper limit at 400 millimoles, per 100 g of the solid matter in the above cationic resin composition. When it is lower than 5 millimoles/100 g, no satisfactory throwing power and curability can be attained and deteriorations may result in hydratability and bath stability. When it exceeds 400 millimoles/100 g, the adhesive resin layer deposition on the conductive material surface will become poor. The sulfonium group content can be

selected within a more preferred range determined according to the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, the above-mentioned lower limit is more preferably 5 millimoles, still more preferably 10 millimoles, and the upper limit is more preferably 250 millimoles, still more preferably 150 millimoles, per 100 g of the solid matter in the cationic resin composition.

The propargyl group in the above cationic resin composition serves as a curable functional group in the cationic electrodepositable adhesive composition. Further, for unknown reasons, the combined use thereof with a sulfonium group can further improve the throwing power of the cationic electrodepositable adhesive composition.

The propargyl group content in the above cationic resin composition should satisfy the condition concerning the total content of the sulfonium and propargyl groups, which is to be described later herein, and, in addition, the lower limit thereto is preferably set at 10 millimoles and the upper limit at 495 millimoles, per 100 g of the solid matter in the above cationic resin composition. When it is lower than 10 millimoles/100 g, no satisfactory throwing power and curability can be attained and, when it exceeds 495 millimoles/100 g, the hydration stability may be adversely affected. The propargyl group content can be selected within a more preferred range according to the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, the above-mentioned lower limit is more preferably 20 millimoles, and the upper limit is more preferably 395 millimoles, per 100 g of the solid matter in the cationic resin composition.

The total content of the sulfonium and propargyl groups in the above cationic resin composition is preferably not higher than 500 millimoles per 100 g of the solid matter in the cationic resin composition. If it exceeds 500 millimoles/100 g, no resin may be actually obtained or no desired performance

characteristics may be obtained. The total content of the sulfonium and propargyl groups in the above cationic resin composition can be selected within a more preferred range according to the resin skeleton employed. In the case of  
5 novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, the total content is more preferably not higher than 400 millimoles.

The propargyl group in the above cationic resin composition may be partly converted to an acetylide. The  
10 acetylide is an acetylene bond-containing metal compound resembling a salt. As for the content of the acetylide-form propargyl group in the above cationic resin composition, the lower limit hereto is preferably 0.1 millimole and the upper limit 40 millimoles, per 100 g of the solid matter in the cationic  
15 resin composition. At content levels below 0.1 millimole, the effect of conversion to acetylides will not be produced to a satisfactory extent and, at content levels exceeding 40 millimoles, the conversion to acetylides is difficult. This content can be selected in a more preferred range according to  
20 the metal species employed.

The metal contained in the above-mentioned acetylide-form propargyl group is not particularly restricted but may be any of those metals which exhibit a catalytic activity, for example copper, silver, barium and other transition metals.  
25 From the viewpoint of applicability to the environment, copper and silver are preferred and, in view of availability, copper is more preferred. When copper is used, the content of the acetylide-form propargyl group in the above cationic resin composition is more preferably 0.1 to 20 millimoles per 100 g  
30 of the solid matter in the cationic resin composition.

Conversion of part of the propargyl group in the above resin composition to an acetylide can result in introduction of a curing catalyst into the resin. By doing so, it becomes unnecessary to use an organic transition metal complex  
35 generally soluble or dispersible only scarcely in organic



solvents and water. Even a transition metal can be readily introduced after conversion to an acetylide into the resin, so that even a scarcely soluble transition metal compound can be freely used. Further, the occurrence of an organic acid salt as an anion in the electrodeposition bath, which is encountered when a transition metal organic acid salt is used, can be avoided and, furthermore, the metal ion will not be removed upon ultrafiltration, hence the bath management and electrodepositable adhesive composition designing become easy.

Where desired, the above cationic resin composition may contain a carbon-carbon double bond. The carbon-carbon double bond is highly reactive, so that the curability can be further improved.

The carbon-carbon double bond content should satisfy the condition concerning the total content of the propargyl group and carbon-carbon double bond, which is to be described later herein, and, in addition, the lower limit thereto is preferably 10 millimoles and the upper limit at 485 millimoles, per 100 g of the solid matter in the above cationic resin composition. When it is lower than 10 millimoles/100 g, no satisfactory curability can be attained by the addition thereof and, when it exceeds 485 millimoles/100 g, the hydration stability may be adversely affected. The carbon-carbon double bond content can be selected within a more preferred range according to the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, the above-mentioned lower and upper limits are preferably 20 millimoles and 375 millimoles, respectively, per 100 g of the solid matter in the cationic resin composition.

When the resin composition contains the above-mentioned carbon-carbon double bond, the total content of the propargyl group and carbon-carbon double bond is preferably within the range from 80 millimoles (lower limit) to 450 millimoles (upper limit) per 100 g of the solid matter in the resin composition.

At content levels lower than 80 millimoles/100 g, the curability may be unsatisfactory and, at levels exceeding 450 millimoles/100 g, the sulfonium group content becomes decreased and the throwing power may become insufficient. The above total  
5 content of the propargyl group and carbon-carbon double bond can be selected within a more preferred range according to the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, the above mentioned lower and upper limits are more preferably 100  
10 millimoles and 395 millimoles, respectively, per 100 g of the solid matter in the cationic resin composition.

When the resin composition contains the above carbon-carbon double bond, the total content of the above sulfonium and propargyl groups and carbon-carbon double bond  
15 is preferably not higher than 500 millimoles per 100 g of the solid matter in the resin composition. When it exceeds 500 millimoles/100 g, no resin can be actually obtained or some or other desired performance characteristics may be no longer obtained. The above total content of the sulfonium and  
20 propargyl groups and carbon-carbon double bond can be selected within a more preferred range according to the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for instance, it is preferably not higher than 400 millimoles per 100 g of the solid matter in the  
25 cationic resin composition.

The above cationic resin composition can suitably be produced, for example, by the step (i) of reacting an epoxy resin having at least two epoxy groups in each molecule with a compound having a functional group capable of reacting with the epoxy  
30 group and, further, a propargyl group to give a propargyl group-containing epoxy resin composition and the step (ii) of reacting the residual epoxy groups in the propargyl group-containing epoxy resin composition obtained in step (i) with a sulfide/acid mixture for sulfonium group introduction.

35 The above-mentioned compound having a functional group

capable of reacting with the epoxy group and, further, a propargyl group (hereinafter referred to as "compound (A)") may be, for example, a compound having both a functional group capable of reacting with the epoxy group, such as a hydroxyl or carboxyl group, and a propargyl group. As specific examples, there may be mentioned propargyl alcohol and propargylic acid, among others. Among these, propargyl alcohol is preferred in view of its availability and good reactivity.

For providing the cationic resin composition with a carbon-carbon double bond according to need, a compound having a functional group capable of reacting with the epoxy group and, further, a carbon-carbon double bond (hereinafter referred to as "compound (B)") is used in combination with the above-mentioned compound (A). The compound (B) may be a compound having both a functional group capable of reacting with the epoxy group, such as a hydroxyl or carboxyl group, and a carbon-carbon double bond. Specifically, when the group reacting with the epoxy group is a hydroxyl group, there may be mentioned 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, allyl alcohol, methallyl alcohol, and the like. When the group reacting with the epoxy group is a carboxyl group, there may be mentioned, among others, acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, phthalic acid, itaconic acid; half esters such as maleic acid ethyl ester, fumaric acid ethyl ester, itaconic acid ethyl ester, succinic acid mono(meth)acryloyloxyethyl ester, and phthalic acid mono(meth)acryloyloxyethyl ester; oleic acid, linolic acid, ricinolic acid, and like synthetic unsaturated fatty acids; and linseed oil, soybean oil, and like nature-derived unsaturated fatty acids.

In the above step (i), the epoxy resin having at least two epoxy groups in each molecule is reacted with the above compound (A) to give a propargyl group-containing epoxy resin

composition or with the above compound (A) and the above compound (B) as necessary to give a propargyl group- and carbon-carbon double bond-containing epoxy resin composition. In the latter case, in the step (i), the compound (A) and compound  
5 (B) may be mixed together in advance and then subjected to reaction, or the compound (A) and compound (B) may be separately subjected to reaction. That functional group reacting with the epoxy group which the compound (A) has and that functional group reacting with the epoxy group which the compound (B) has may  
10 be the same or different.

When, in the above step (i), the compound (A) and compound (B) are subjected to reaction with the epoxy resin, the proportion between both compounds may be selected so that a desired functional group content may be obtained, for example  
15 that the above-mentioned propargyl group and carbon-carbon double bond contents may be obtained.

As for the reaction conditions in the above step (i), the reaction is generally carried out at room temperature or 80 to 140°C for several hours. If necessary, one or more known  
20 ingredients necessary for the progress of the reaction, such as a catalyst and/or solvent, may be used. The completion of the reaction can be checked by epoxy equivalent determination, and the functional group introduced can be confirmed by analysis of nonvolatile fraction and instrumental analysis of the resin  
25 composition obtained. The thus-obtained reaction product generally occurs as a mixture of epoxy resins having one or a plurality of propargyl groups, or a mixture of epoxy resins having one or a plurality of propargyl groups and carbon-carbon double bonds. In this sense, the resin composition obtained  
30 in the above step (i) is a propargyl group-containing one or a propargyl group- and carbon-carbon double bond-containing one.

In the step (ii), the residual groups in the propargyl group-containing epoxy resin composition obtained in the above  
35 step (i) are reacted with a sulfide/acid mixture for sulfonium

group introduction. This introduction of the sulfonium group can be effected by the method which comprises causing the sulfide/acid mixture to react with the epoxy group to effect introduction of the sulfide and conversion thereof to the sulfonium group or the method which comprises introducing a sulfide and then converting the introduced sulfide to a sulfonium group with an acid, an alkyl halide, such as methyl fluoride, methyl chloride or methyl bromide, or the like reagent, if necessary, followed by anion exchange. In view of the availability of the reactant, the method using a sulfide/acid mixture is preferred.

The above sulfide is not particularly restricted but includes, among others, aliphatic sulfides, aliphatic-aromatic mixed sulfides, aralkyl sulfides, and cyclic sulfides. Specifically, there may be mentioned, for example, diethyl sulfide, dipropyl sulfide, dibutyl sulfide, dihexyl sulfide, diphenyl sulfide, ethyl phenyl sulfide, tetramethylene sulfide, pentamethylene sulfide, thiodiethanol, thiodipropanol, thiodibutanol, 1-(2-hydroxyethylthio)-2-propanol, 1-(2-hydroxyethylthio)-2-butanol, and 1-(2-hydroxyethylthio)-3-butoxy-1-propanol.

The above-mentioned acid is not particularly restricted but includes, among others, formic acid, acetic acid, lactic acid, propionic acid, boric acid, butyric acid, dimethylolpropionic acid, hydrochloric acid, sulfuric acid, phosphoric acid, N-acetylglycine, and N-acetyl- $\beta$ -alanine.

The mixing ratio between the sulfide and acid in the above sulfide/acid mixture is generally and preferably about 100/40 to 100/100 as expressed in terms of sulfide/acid mole ratio.

The reaction in the above step (ii) can be carried out, for example, by mixing the propargyl group-containing epoxy resin composition obtained in the above step (i) and the above sulfide/acid mixture in an amount selected so as to give the above-mentioned sulfonium group content, for instance, with

water in an amount of 5 to 10 moles per mole of the sulfide used and stirring the mixture generally at 50 to 90°C for several hours. A residual acid value of 5 or below may serve as a criterion in judging the reaction to be at the end point. The sulfonium group introduction in the resin composition obtained  
5 can be confirmed by potentiometric titration.

The same procedure can be used also in the case where the sulfide is first introduced and then converted to the sulfonium group. By carrying out introduction of the sulfonium group after  
10 introduction of the propargyl group, as mentioned above, the sulfonium group can be prevented from being decomposed upon heating.

When the propargyl group in the above resin composition is partly converted to an acetylide, conversion to the  
15 acetylide can be carried out by the step of reacting the propargyl group-containing epoxy resin obtained in the above step (i) with a metal compound to thereby convert part of the propargyl group in the above-mentioned epoxy resin composition to the corresponding acetylide. The metal compound is  
20 preferably a transition metal compound capable of giving an acetylide and includes, among others, complexes or salts of such transition metals as copper, silver and barium. Specifically, there may be mentioned, for example, acetylacetonato-copper, copper acetate, acetylacetonato-silver, silver acetate,  
25 silver nitrate, acetylacetonato-barium, and barium acetate. Among these, copper or silver compounds are preferred from the environmental friendliness viewpoint, and copper compounds are more preferred because of their ready availability. For example, acetylacetonato-copper is suitably used in view of the  
30 ease of bath control.

As regards the reaction conditions for converting partly the propargyl group to an acetylide, the reaction is generally carried out at 40 to 70°C for several hours. The progress of the reaction can be checked by the coloration of the resulting  
35 resin composition and/or the disappearance of the methine

proton signal on a nuclear magnetic resonance spectrum. The time when the propargyl group-derived acetylide in the cationic resin composition arrives at a desired level is thus determined and, at that time, the reaction is terminated. The reaction product obtained is generally a mixture of epoxy resins with one or a plurality of propargyl groups converted to an acetylide. A sulfonium group can be introduced, by the above step (ii), into the thus obtained epoxy resin composition with the propargyl group partly converted to an acetylide.

The step of partly converting the propargyl group in the epoxy resin composition to an acetylide and the step (ii) can be carried out under common reaction conditions, so that both steps can be carried out simultaneously. The production process can be advantageously simplified by carrying out both steps simultaneously..

In this way, the propargyl group- and sulfonium group-containing resin composition optionally containing a carbon-carbon double bond and/or a propargyl group-derived acetylide according to need can be produced while preventing the sulfonium group from being decomposed. Although acetylides in a dry state are explosive, the reaction in the practice of the invention is carried out in an aqueous medium and the desired substance can be obtained in the form of an aqueous composition. Therefore, there arises no safety problem.

Since the above-mentioned cationic electrodepositable adhesive composition comprises the above-mentioned cationic resin composition and the cationic resin composition itself is curable, it is not always necessary to use the cationic electrodepositable adhesive composition. However, for further improving the curability, a curing agent may be used. As such curing agent, there may be mentioned, among others, compounds having a plurality of propargyl groups and/or carbon-carbon double bonds, for example compounds obtained by subjecting a propargyl group-containing compound, such as

propargyl alcohol, or a carbon-carbon double bond-containing compound, such as acrylic acid, to addition reaction to a novolak phenol- or like compound-derived polyepoxide or pentaerythritol tetraglycidyl ether.

5 It is not always necessary to use the cationic electrodepositable adhesive composition in the above cationic electrodeposition coating composition. However, when a further improvement in curability is required depending on the curing reaction conditions, a transition metal compound in  
10 general use, for instance, may be added in an appropriate amount according to need. Such compound is not particularly restricted but includes, among others, complexes or compounds resulting from combination with a ligand, such as cyclopentadiene or acetylacetone, or a carboxylic acid, such as acetic acid, to  
15 transition metals such as nickel, cobalt, manganese, palladium, and rhodium. The level of addition of the above curing catalyst is preferably from 0.1 millimole (lower limit) to 20 millimoles (upper limit) per 100 g of the resin solids in the cationic electrodepositable adhesive composition.

20 An amine may further be incorporated in the above cationic electrodepositable adhesive composition. By the addition of the amine, the conversion of the sulfonium group to a sulfide by electrolytic reduction in the process of electrodeposition is increased. The amine is not particularly restricted but  
25 includes, among others, amine compounds such as primary to tertiary monofunctional or polyfunctional aliphatic amines, alicyclic amines and aromatic amines. Among these, water-soluble or water-dispersible ones are preferred and, thus, mention may be made of C<sub>2-8</sub> alkylamines such as monomethylamine,  
30 dimethylamine, trimethylamine, triethylamine, propylamine, diisopropylamine and tributylamine; monoethanolamine, dimethanolamine, methylethanolamine, dimethylethanolamine, cyclohexylamine, morpholine, N-methylmorpholine, pyridine, pyrazine, piperidine, imidazoline, imidazole and the like.  
35 These may be used singly or two or more of them may be used in



combination. Among them, hydroxy amines such as monoethanolamine, diethanolamine and dimethylethanolamine are preferred from the view point of excellent dispersion stability in water.

5       The above amine can be directly incorporated in the above cationic electrodepositable adhesive composition.

      The level of addition of the above amine is preferably 0.3 milliequivalents (meq) (lower limit) to 25 meq (upper limit) per 100 g of the resin solid matter in the cationic  
10   electrodepositable adhesive composition. If it is less than 0.3 meq/100 g, any sufficient effect on the throwing power cannot be obtained. If it exceeds 25 meq/100 g, the effects proportional to the addition level can no longer be obtained; this is not economical. The lower limit is more preferably 1  
15   meq/100 g, and the upper limit is more preferably 15 meq/100 g.

      In the above cationic electrodepositable adhesive composition, there may be incorporated an aliphatic hydrocarbon group-containing resin composition. The incorporation of the  
20   aliphatic hydrocarbon group-containing resin composition improves the impact resistance of the adhesive resin layer after curing. The aliphatic hydrocarbon group-containing resin composition includes those containing, per 100 g of the solid matter in the resin composition, 5 to 400 millimoles of a  
25   sulfonium group, 80 to 135 millimoles of a C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, and 10 to 315 millimoles of at least one of an unsaturated double bond-terminated C<sub>3-7</sub> organic group and a propargyl group, with the total content of  
30   the sulfonium group, the C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, the unsaturated double bond-terminated C<sub>3-7</sub> organic group and the propargyl group being not higher than 500 millimoles per 100 g of the solid matter in the resin  
35   composition.

When such aliphatic hydrocarbon group-containing resin composition is incorporated in the above-mentioned cationic electrodepositable adhesive composition, each 100 g of the resin solid matter in the cationic electrodepositable adhesive composition preferably contains 5 to 400 millimoles of the sulfonium group, 10 to 300 millimoles of the C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, and 10 to 485 millimoles of the propargyl group and unsaturated double bond-terminated C<sub>3-7</sub> organic group in total, the total content of the sulfonium group, the C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, the propargyl group and the unsaturated double bond-terminated C<sub>3-7</sub> organic group is preferably not higher than 500 millimoles per 100 g of the resin solid matter in the cationic electrodepositable adhesive composition, and the content of the above C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, is preferably 3 to 30% by mass based on the resin solid matter in the cationic electrodepositable adhesive composition.

In cases where the aliphatic hydrocarbon group-containing resin composition is incorporated in the above cationic electrodepositable adhesive composition, when the sulfonium group content is below 5 millimoles/100 g, no sufficient throwing power and curability can be exhibited and deteriorations in hydratability and bath stability will result. When it exceeds 400 millimoles/100 g, the adhesive resin layer deposition on the conductive material surface becomes poor. When the content of the C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, is less than 80 millimoles/100 g, the improvement in impact resistance will be unsatisfactory and, when it exceeds 350 millimoles/100 g, the resin composition becomes difficult to handle. When the total content of the propargyl group and the C<sub>3-7</sub> unsaturated double bond-terminated organic group is

lower than 10 millimoles/100 g, no satisfactory curability will be produced even when another resin and/or a curing agent is used combinedly. When it exceeds 315 millimoles/100 g, the impact resistance will be improved only to an unsatisfactory extent. The total content of the sulfonium group, the C<sub>8-24</sub> aliphatic hydrocarbon group, which may optionally contain an unsaturated double bond in the chain thereof, the propargyl group and the C<sub>3-7</sub> unsaturated double bond-terminated organic group is not more than 500 millimoles per 100 g of the solid matter in the cationic resin composition. When it exceeds 500 millimoles, no resin will be actually obtained or the desired performance characteristics may not be obtained.

The above cationic electrodepositable adhesive composition can be prepared, for example, by admixing the above cationic resin composition with the above-mentioned other ingredients according to need and dissolving or dispersing the resulting composition in water. On the occasion of use in the electrodeposition step, the bath solution/dispersion prepared preferably has a nonvolatile matter content of 10% by mass (lower limit) to 30% by mass (upper limit). The preparation is preferably carried out so that the contents of the propargyl group, carbon-carbon double bond and sulfonium group in the cationic electrodepositable adhesive composition may not deviate from the respective ranges indicated hereinabove referring to the resin composition.

The above-mentioned conductive material to be used in the above step (1) is not particularly restricted but may be any of those substrates in sheet/plate or firm-like form which show electric conductivity for enabling the electrodeposition coating step, for example metal moldings, such as sheets or plates and molded articles, made of iron, copper, aluminum, gold, silver, nickel, tin, zinc, titanium, tungsten or the like, or an alloy containing such metals. Two conductive materials forming the laminate obtained by the method of producing a laminate may be the same or different. In the case of a sulfonium

group- and propargyl group-containing cationic resin composition, conductive materials made of copper, aluminum or iron or an alloy comprising these as main constituents are more preferred, since sulfur atom-metal atoms in the conductive material surface bonds are readily formed with them.

As the method of carrying out the electrodeposition step in the above step (1), there may be mentioned, for example, the method comprising immersing the above conductive material in the above cationic electrodepositable adhesive composition for utilizing the conductive material as a cathode, and applying a voltage generally within the range of 50 to 450 V between the cathode and anode. When the voltage applied is lower than 50 V, insufficient electrodeposition will result. At a voltage exceeding 450 V, the electricity consumption uneconomically increases. When the above cationic electrodepositable adhesive composition is used and a voltage within the above range is applied, a uniform adhesive resin layer can be formed on the whole conductive material surface, without any rapid increase in film thickness in the process of electrodeposition. In ordinary cases, the cationic electrodepositable adhesive composition bath temperature when the above voltage is applied is preferably 10 to 45°C. On the other hand, the voltage application time may vary depending on the electrodeposition conditions but, generally, it may be 0.3 second to 4 minutes.

In the method of producing a laminate of the invention, a drying step may be carried out after conducting the above electrodeposition step. The drying step is the step of heating the conductive material with an adhesive resin layer formed thereon in a temperature range within which no curing reaction occurs. When such drying is conducted, the volatile materials, such as the solvent, remaining in the adhesive resin layer can be thoroughly removed to attain further improvement and uniformity in adhesion strength and insulation. The above drying is preferably carried out by heating within a temperature range from a lower limit of room temperature, preferably a lower

limit of 50°C, to an upper limit of 100°C for 5 to 20 minutes.

The second step in method of producing a laminate of the invention is the step (2) of joining the adhesive resin layer on each conductive material as obtained in the step (1) to each side of a functional material. By joining two conductive materials each having the adhesive resin layer obtained in the above step (1) to the functional material, it is possible to obtain a laminate having a laminate structure such as shown in Fig. 1 by way of example.

The above functional material is not particularly restricted but may be any of those materials having a sheet/plate or film-like form and capable of performing a certain function in the field of electronic materials, including, for example, those conductive materials used in the above step (1), plastics moldings and other organic materials, inorganic materials, foamed or expanded articles, and the like.

The above organic materials are not particularly restricted but include, for example, plates and other moldings made of polypropylene resins, polycarbonate resins, urethane resins, polyester resins, polystyrene resins, ABS resins, vinyl chloride resins, polyamide resins, and so on.

The above inorganic materials are not particularly but include barium titanate and the like.

The above step (2) preferably comprises a heating/adhesion step and a heating/curing step. The heating/adhesion step is the step of heating insufficient for causing the curing reaction of the adhesive resin layer but sufficient for melting the adhesive resin layer and attaching thereto the functional material. This brings the conductive material and the functional material into close contact with each other. In cases where the conductive material and functional material each has an adhesive resin layer on the adhesive surface, both the adhesive resin layers are melted and fused together in the above heating/adhesion step to give one uniform adhesive layer. Such a uniform adhesive layer

resulting from fusion contributes to further improvement in adhesion strength.

As for the heating conditions in the above heating/adhesion step, the heating is preferably carried out at 70 to 200°C for several seconds to several tens of seconds. Heating below the above lower limits may fail to attain satisfactory intimate adhesion between the conductive material and functional material. Heating exceeding the above upper limits allows the adhesive resin layer to cure before close adhesion thereof to the functional material, so that the adhesion strength may decrease.

The above heating/curing step is the step of firmly brining the adhesive resin layer of each conductive material and the functional material into close contact and curing the adhesive resin layer by further heating to thereby attain firm adhering the adhesive resin layer to the functional material as a result of curing.

As for the heating conditions in the above heating/curing step, the adhesive resin layer-mediated firm adhering the conductive material to functional material can be attained by curing the adhesive resin layer by heating at 120 to 260°C, preferably at 160 to 240°C, for 10 to 30 minutes. Heating below the above lower limits may result in insufficient curing, hence in a decrease in adhesion strength. Heating exceeding the above upper limits will produce no further improvement in adhesion strength, hence may be uneconomical. The above heating/adhesion step and heating/curing step may be carried out successively.

The above step (2) is preferably carried out using a vacuum press apparatus. When the conductive material and functional material are joined together using a vacuum press apparatus, bubbles contained in the adhesive resin layer in the step of joining can be eliminated. Thus, the adhesion strength of the resulting laminate can be further improved.

The above-mentioned vacuum press apparatus may be any of

those known in the art.

In the above step (2), both the adhesive resin layer-carrying conductive materials may be joined simultaneously to both sides of the functional material, or one  
5 of the conductive materials may be first joined to one side of the functional material and, after curing/heating, the other conductive material may be joined to the other side.

The above functional material may have an adhesive resin layer on one side or on each side. The adhesive resin layer  
10 of the above functional material is not particularly restricted but may be an adhesive resin layer well known to those skilled in the art, for example a layer resulting from application of an adhesive in conventional use. However, it is desirable, particularly when the above functional material is the above  
15 conductive material, that a conductive material having an adhesive resin layer(s) obtained by carrying out the above-mentioned step (1) be used as the functional material. In this case, the adhesive resin layers can be brought into contact with each other and then cured and, after curing, there  
20 is formed a covalent bond-like state resulting from strong interaction between the respective conductive materials and the adhesive resin layer and, as a result, the adhesion strength can be further improved.

When the above-mentioned functional material is such a  
25 organic material or inorganic material as mentioned above, the laminate obtained by the above-mentioned method of producing a laminate can be adequately used as a capacitor.

The laminate obtained by the above-mentioned method of producing a laminate is high in the adhesion strength between  
30 each conductive material and the functional material and the cured adhesive resin layer formed between each conductive material and the functional material is excellent in insulating properties and, therefore, such laminate can be adequately used in the field of electronic materials. Such laminate also  
35 constitutes an aspect of the present invention.

Method of producing a laminate of the present invention comprises the step (1) of forming, on each of two conductive materials, an adhesive resin layer by carrying out an electrodeposition step using a cationic electrodepositable adhesive composition comprising a cationic resin composition and the step (2) of joining the adhesive resin layer on each conductive material as obtained in the step (1) to each side of a functional material. In particular, when the above cationic electrodepositable adhesive composition has functional groups capable of interacting with the metal atoms in the conductive material surface in the step of joining, or when it releases substantially no volatile matter in the step of curing by heating, laminates more improved in insulating properties and adhesion strength between the conductive materials and functional material can be obtained. Furthermore, when the cationic resin composition is an unsaturated bond-containing one, such effects are still more improved. When the conductive material is plates or other moldings made of metal and the cationic resin composition is a sulfonium group- and propargyl group-containing one, the adhesive resin layer formed has the sulfonium groups and, therefore, strong interaction presumably occurs between the sulfur atoms and the metal atoms in the conductive material surface, leading to formation of a covalent bond-like state after curing by heating. This can result in firmer adhesion adhering and, further, in still better insulating properties. It is essential that an electrochemical reaction be induced by voltage application in the electrodeposition step; mere heating alone cannot allow the curing reaction to proceed. Accordingly, it is superior in stability as well. Therefore, the above-mentioned method of producing a laminate can be adequately utilized in the field of electronic materials.

Method of producing a laminate of the invention, which has the constitution described hereinabove, can give laminates



high in adhesion strength. Therefore, method of producing a laminate of the invention can be adequately used in the field of electronic materials, and the laminates obtained can be adequately used as capacitors or like electronic parts.

5

#### EXAMPLES

The following examples illustrate the present invention more specifically. These examples are, however, by no means limitative of the scope of the invention. In the examples,  
10 "part(s)" means "parts by mass", unless otherwise specified.

##### Production Example 1

Production of a sulfonium group- and propargyl group-containing epoxy resin composition

15       Epototo YDCN-701 (100.0 parts) with an epoxy equivalent of 200.4 (cresol novolak-based epoxy resin, product of Toto Chemical), 23.6 parts of propargyl alcohol, and 0.3 part of dimethylbenzylamine were placed in a separable flask equipped with a stirrer, thermometer, nitrogen inlet tube and reflux  
20 condenser, the mixture was heated to 105°C, and the reaction was allowed to proceed at that temperature for 3 hours to give a propargyl group-containing resin composition with an epoxy equivalent of 1,580. To this was added 2.5 parts of acetylacetonato-copper, and the reaction was allowed to proceed  
25 at 50°C for 1.5 hours. It was confirmed that part of the terminal hydrogens of the added propargyl groups was disappeared by proton (1H) NMR (propargyl converted to acetylide: 14 millioles/100 g of the resin solid matter). To this were added 10.6 parts of  
30 1-(2-hydroxyethylthio)-2,3-propanediol, 4.7 parts of glacial acetic acid and 7.0 parts of deionized water, and the reaction was allowed to proceed for 6 hours while maintaining the temperature at 75°C. After confirmation that the residual acid value is less than 5, 43.8 parts of deionized water was added  
35 to give a desired resin composition solution. This solution

had a solid matter content of 70.0% by mass, and the sulfonium value was 28.0 millimoles/100 g. The number average molecular weight (determined by GPC on the polystyrene equivalent basis) was 2,443.

5

#### Production Example 2

Production of a cationic electrodepositable adhesive composition

The epoxy resin composition obtained in Production Example 1 (142.9 parts) and 157.1 parts of deionized water were stirred in a high-speed rotary mixer for 1 hour and, then, 373.3 parts of deionized water was further added to prepare an aqueous solution with a solid matter concentration of 15% by mass. An cationic electrodepositable adhesive composition was thus obtained.

15

#### Example 1

[Production of laminate 1]

One surface of each of two 250-mm square aluminum sheets with a thickness of 5 mm was masked with a readily releasable resin-made masking tape for avoiding adhesion sticking thereto. Then, an adhesive resin layer was formed on the other surface by electrodeposition coating with the cationic electrodepositable adhesive composition obtained. Two adhesive resin layer-carrying aluminum sheets were thus obtained.

25

The two adhesive resin layer-carrying aluminum sheets thus obtained were dried in a drying oven with hot air circulation at 90°C for 10 minutes to form dried adhesive resin layers. These dried adhesive resin layers were not tacky at room temperature and became tacky at a temperature above 60°C. In that dried state, the dried adhesive resin layers had a thickness of 15 to 20  $\mu\text{m}$ .

30

The masking tape was peeled off from each dried aluminum sheet, a 65 x 10 mm copper sheet with a thickness of 0.7 mm was

35

sandwiched between the two aluminum sheets with the dried adhesive resin layers facing each other. The three metal sheets were pressed to one another using a vacuum press apparatus set at 190°C to attain lamination and adhesion between the aluminum sheets and copper sheet. The dried adhesive resin layers were then cured by 25 minutes of continued heating at 190°C, whereby a laminate (laminate 1) was obtained. The vacuum press conditions were as follows: 0.5 MPa, 3 seconds. The adhesive resin layer(s) after curing had a thickness of 12 to 20  $\mu\text{m}$ .

#### Example 2

A laminate (laminate 2) was obtained in the same manner as in Example 1 except that a polypropylene sheet (thickness 2 mm, 65 x 10 mm) was used in lieu of the copper sheet.

#### Example 3

A laminate (laminate 3) was obtained in the same manner as in Example 1 except that the copper sheet (thickness 0.7 mm, 65 x 10 mm) having dried adhesive resin layers, on each side, formed by electrodeposition coating with the obtained cationic electrodepositable adhesive composition and dried in a drying oven with hot air circulation at 90°C for 10 minutes was used in lieu of the copper sheet.

#### Example 4

One surface of a 70 x 150 mm iron sheet with a thickness of 0.8 mm was masked with a readily releasable resin-made masking tape for avoiding adhesion sticking thereto. Then, an adhesive resin layer was formed on the other surface by electrodeposition coating with the cationic electrodepositable adhesive composition obtained, whereby an adhesive resin layer-carrying iron sheet was obtained.

The adhesive resin layer of the thus-obtained adhesive resin layer-carrying iron sheet was dissolved using tetrahydrofuran (THF), and a 10 mm square sample was excised

from the sheet.

The surface condition (state of the iron and adhesive resin layer) of this sample was observed using "AXIS-HS" (XPS, product of Shimadzu Corp.). The measurement results are shown in Fig. 2. When the sample as such was measured, the interface between the residual coating film and iron could not be observed because the thickness of that film was greater than the depth of analysis. A peak (163.7 eV) ascribable to the sulfide occurring in the coating film was observed. After removal, to a certain extent, of the coating film by sputtering, the interface with iron became analyzable and a peak (161.9 eV) ascribable to S-Fe was observed. From these results, it was revealed that interaction (between S and Fe) occurred between the adhesive resin layer formed and the iron sheet and a covalent bond-like state was formed in the electrodeposition coating.

#### Comparative Examples 1 to 3

Laminates 4 to 6 were obtained in the same manner as in Examples 1 to 3, respectively, except that Powertop U-30 (blocked isocyanate curing type epoxy resin-based cationic electrodeposition adhesive, product of Nippon Paint Co.) was used in lieu of the cationic electrodepositable adhesive composition obtained in Production Example 2.

#### [Evaluation]

The thus-obtained laminates 1 to 6 were measured for peel adhesion strength upon peeling at 90° using a Shimadzu model AGS-100 autograph. The measurement conditions were as follows: pulling speed 5 mm/minute, 20°C.

Table 1

5

	Example			Comparative Example		
	1	2	3	1	2	3
Peel adhesion strength upon peeling at 90° (kN/m)	12	1.5	14	0.7	0.4	0.7

As is apparent from Table 1, the laminates obtained in Examples 1 to 3 were higher in adhesion strength than those obtained in Comparative Examples 1 to 3.

10

## CLAIMS

1. A method of producing a laminate  
which comprises the step (1) of forming, on each of two  
5 conductive materials, an adhesive resin layer by an  
electrodeposition step with a cationic electrodepositable  
adhesive composition comprising a cationic resin composition  
and the step (2) of joining the adhesive resin layer on each  
conductive material as obtained in the step (1) to each side  
10 of a functional material.

2. The method of producing a laminate according to Claim  
1,  
wherein the cationic electrodepositable adhesive  
15 composition is substantially incapable of generating any  
volatile component in the step of heating for curing.

3. The method of producing a laminate according to Claim  
1 or 2,  
20 wherein the cationic resin composition is an unsaturated  
bond-containing one.

4. The method of producing a laminate according to any  
of Claim 1 to 3,  
25 wherein the cationic resin composition is one allowing  
the formation, in the adhesive resin layer, of such chemical  
species activated by the electrode reaction caused by voltage  
application in the electrodeposition step as can promote the  
progress of the curing reaction.

5. The method of producing a laminate according to any  
of Claim 1 to 4,  
wherein the cationic resin composition is a sulfonium  
group- and propargyl group-containing one.

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6. The method of producing a laminate according to any of Claim 1 to 5,

wherein the cationic resin composition has a sulfonium group content of 5 to 400 millimoles, a propargyl group content of 10 to 495 millimoles, and a total content of sulfonium and propargyl groups of not more than 500 millimoles, per 100 g of the solid matter in the cationic resin composition.

7. The method of producing a laminate according to any of Claim 1 to 6,

wherein the cationic resin composition has a sulfonium group content of 5 to 250 millimoles, a propargyl group content of 20 to 395 millimoles, and a total content of sulfonium and propargyl groups of not more than 400 millimoles, per 100 g of the solid matter in the cationic resin composition.

8. The method of producing a laminate according to any of Claim 1 to 7,

wherein the cationic resin composition has an epoxy resin as a skeleton.

9. The method of producing a laminate according to any of Claim 1 to 8,

wherein the epoxy resin is a novolak cresol epoxy resin or novolak phenol epoxy resin and has a number average molecular weight of 700 to 5,000.

10. The method of producing a laminate according to any of Claim 1 to 9,

which comprises a step of drying between the step (1) and step (2).

11. The method of producing a laminate according to any of Claim 1 to 10,

wherein the step (2) comprises a step of adhesion with

heating and a step of curing by heating.

12. The method of producing a laminate according to any of Claim 1 to 11,

5        wherein the functional material is made of an organic or inorganic material.

13. A laminate obtained by the method of producing a laminate according to any of Claim 1 to 12.

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Fig.1

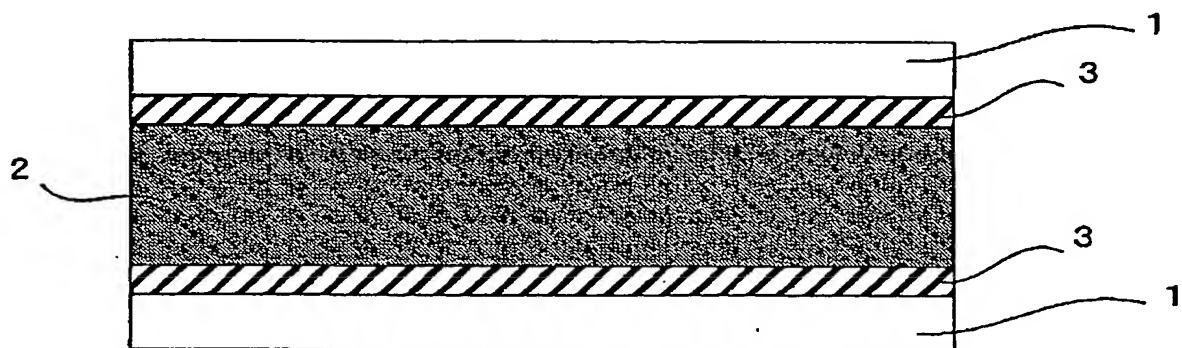
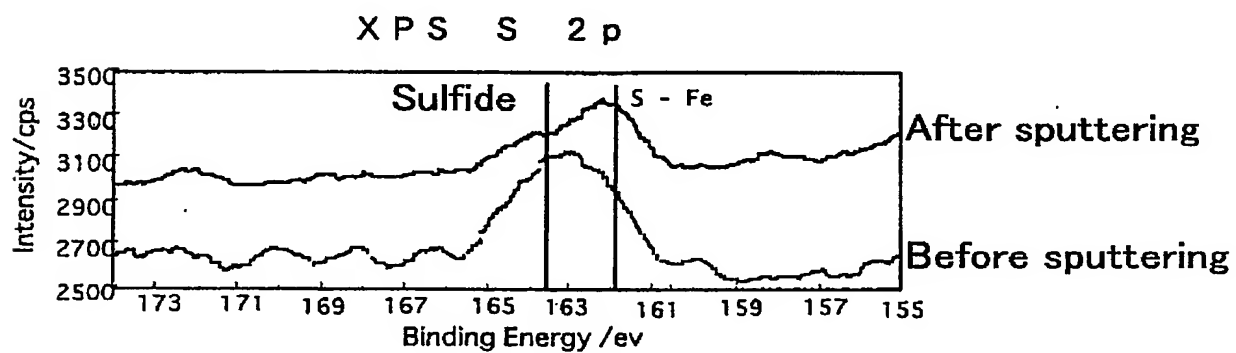


Fig.2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/ 11865

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>7</sup> B32B 15/08, C09J 5/00, C09J 9/02, B05D 1/04, B05D 7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>7</sup> B32B 15/08, C09J 5/00, C09J 9/02, B05D 1/04, B05D 7/24, C09J 157/00, C09J 163/10, C09D 5/44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 Japanese Utility Model Gazette 1926-1996, Japanese Publication of Unexamined Utility Model Applications 1971-2003, Japanese Registered Utility Model Gazette 1994-2003, Japanese Gazette Containing the Utility Model 1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI/L

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5676812 A (CANON KABUSHIKI KAISHA) 1997.10.14, ALL DOCUMENT & JP 4-212498 A	1-4, 8 5-7, 9-13
X Y	JP 3-112190 A (MATSUSHITA DENKO KAISHA) 1991.05.13, ALL DOCUMENT (NO FAMILIES)	1-4, 8 5-7, 9-13
Y	EP 854207 A1 (NIPPON PAINT CO., LTD.) 1998.07.22, ALL DOCUMENT & EP 852252 A1 & JP 3259274 B2 & US 6106684 A	1-13
Y	EP 974624 A2 (NIPPON PAINT CO., LTD.) 2000.01.26, ALL DOCUMENT & JP 2000-38527 A	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

15.01.2004

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/ 11865

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 49-102726 A (MATSUSHITA) 1974.09.27, ALL DOCUMENT (NO FAMILIES)	1-13
Y	JP 9-157621 A (JAPAN ENERGY KABUSHIKI KAISHA) 1997.06.17, ALL DOCUMENT (NO FAMILIES)	1-13
Y	EP 458296 A2 (NIPPON PAINT CO., LTD.) 1991.11.27, ALL DOCUMENT & JP 4-28712 A & US 5242996 A	1-13